

THE APPLICATION OF FOURIER TRANSFORM INFRARED SPECTROSCOPY  
TO THE CHARACTERIZATION OF COAL STRUCTURE

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INTRODUCTION

Infrared spectroscopy is an important and widely used analytical tool for determining the structure of organic materials. Most of the fundamental work on applying this technique to coal characterization was performed in the 1950's and 1960's and has been reviewed in a number of articles (1-4). These studies were limited by two major problems. First, coal absorbs strongly in the infrared so that in conventional dispersive instruments only a weak signal reaches the detector, producing relatively poor spectra. Second, the overlap and superposition of the absorption bands of such complex multicomponent systems result in spectra consisting of broad features with little fine structure, so that only a general, mainly qualitative, identification of a few functional groups has so far been possible.

The introduction of computerized Fourier transform infrared spectrometers opens up new possibilities for the spectroscopic characterization of coal and coal derived liquids. There are several advantages of FTIR compared to dispersive instruments, discussed in detail in a number of reviews (5-7). Essentially, the use of an interferometer rather than a system of gratings and slits results in a higher energy throughput to the detector. This, coupled with the ability of such internally calibrated computerized systems to co-add a large number of interferograms, results in markedly superior spectra, particularly in the energy limiting situations encountered in coal studies. The resulting multiplexed spectrum can then be scale-expanded by the computer to display subtle features without undue interference from background noise. However, in coal studies it has been our experience that the most significant results can be obtained by applying the types of computer routines that have recently become associated with FTIR, particularly spectral subtraction and least squares curve fitting. In fact, the first application of FTIR to the characterization of coal in this laboratory depended more on such computer manipulations than on the enhanced sensitivity of these instruments. Methods for the complete analysis of the major mineral components present in coal have been developed (8-11). We have also applied FTIR to a number of problems concerning the organic structure of coal, including studies of solvent refined coal (12) and the changes that occur upon carbonization (13) and oxidation (14,15). In this communication we will initially discuss the application of recently introduced FTIR computer routines to the quantitative determination of species present in coal, both inorganic and organic. We will then conclude by considering the utility of these methods in determining variations in structure as a function of position in a seam.

RECENT DEVELOPMENTS IN THE ANALYSIS OF MINERAL MATTER IN COAL BY FTIR

Recent work in this laboratory has demonstrated that FTIR offers considerable potential for quantitatively determining the major mineral components present in coal or, more precisely, present in the low temperature ash (LTA) (8-11).

Essentially, the procedure consists of the successive subtraction of the spectra of mineral "standards" from the spectrum of the LTA. As the bands of the most prevalent or most highly absorbing minerals are removed, those of the weakly absorbing or less prevalent components are revealed, allowing a more complete and accurate analysis. It was found that all major components (those constituting at least 3-4% by weight) could be determined, providing that appropriate mineral "standards" are available.

Despite the obvious potential and advantages of the FTIR method, there are still major problems. Perhaps the most critical of these is the availability of suitable standards. This problem is particularly acute in the analysis of clays, but not one unique to FTIR since other methods also rely on standards for calibration of band and line intensities. One solution to this problem that is particularly suited to FTIR is the compilation of an extensive mineral library, because spectra of these materials can be routinely and conveniently stored on disk or magnetic tape and recalled at any future time. We are in the process of building such a library, but it is already apparent that we have in some respects substituted one problem for another. How do we choose the "correct" or most appropriate standard for a particular analysis? For example, we have kaolinite samples from different geographic localities that differ subtly in their spectra according to parameters such as degree of crystallinity. Finally, even if by luck or judgement we choose an appropriate mineral spectrum for a particular analysis, the accuracy of the FTIR method is limited by the essentially subjective judgement of when bands have been exactly subtracted from a spectrum. Such errors are not large for major components having strong well resolved bands, but can become critical in determining low concentrations of certain species. We believe that the application of least squares curve fitting programs, first described by Koenig and co-workers (16), offer at least a partial solution.

The utility of the method is best illustrated by a simple example. Figure 1 compares the FTIR spectra of three individual clays. Also included is the spectrum of a mixture of these three clays, which (as noted above) is extremely difficult to quantitatively analyze by other methods. The least squares program was then asked to fit the spectra of seven standards to the spectrum of the mixture. We deliberately included spectra of mineral standards that we knew were not contained in the synthetic mixture in order to test the utility and accuracy of the procedure. The results are shown in Table 1 and the resulting "composite" spectrum is compared to that of the original mixture in Figure 2. The composite spectrum was constructed by adding the spectra of the components weighted according to the parameters determined in the least squares analysis. Not only did the program pick the correct clays in spite of the similarity in their spectra, but also was able to distinguish between two kaolinites from different origins. This latter result was somewhat of a surprise because the spectra of the two kaolinites are extremely similar, as can be seen from Figure 3, differing only slightly in the relative intensities of one or two bands. In addition to quickly and conveniently "picking" the right components, the program also gave directly a quantitative measure of the clays present that is in very good agreement with the weighed quantities. (This direct measure was possible because we normalized all spectra by dividing them by a number equal to the weight of material in the KBr pellet.) The analysis can be improved by then rejecting all components with minor and negative contributions to the fit. Clearly, if we are examining a low temperature ash we would then have to check that we were not eliminating a true minor component by subtracting the spectrum of the major components from that of the ash (using the subtraction parameters also determined by the least squares fit program).

In applying this technique to the analysis of an LTA we use the least squares curve-fitting procedure to first pick the "best" standards from a given set. As in the analysis of the simple mixtures we can then reject those mineral spectra that have negative subtraction coefficients (but not necessarily those with the small positive contributions) and repeat the fit. The least squares coefficients, (corresponding to the subtraction parameters) determined by this final analysis are then a quantitative measure of the contribution of each mineral. Finally, a check on the accuracy of the results can be obtained by sequentially subtracting the spectrum of each component. This ensures that minor components have not been inadvertently ignored.

Although this procedure sounds tedious, these tasks are in fact performed rou-

tinely and quickly by the FTIR mini-computer. As an example we will consider the results of the analysis of the LTA of an Illinois #6 coal, as presented in Table 2. The percentage weight fraction figures were taken directly from the solution vector. Two clays were determined to have a negative contribution, one of them to our initial surprise was the Illinois kaolinite. Our preconceptions were that an Illinois kaolinite would be the best standards for an analysis of an Illinois coal. However, the fundamental difference in these two standards is probably the degree of crystallinity (11). Consequently, the kaolinite in this sample appears to have a degree of crystallinity that is better approximated by the Georgia kaolinite. The least squares fit was repeated after the removal of the Illinois kaolinite and illite spectra from the refinement. These results are also presented in Table 2 where they are compared to the results taken from traditional infrared and x-ray methods. It can be seen that there is good agreement for those minerals determined by both techniques. However, traditional procedures were not capable of accurately determining clays, whereas the FTIR method does provide what appears to be a reasonable analysis of these materials.

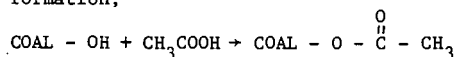
We did not determine pyrite by FTIR because this mineral does not have absorption bands in the spectral range ( $1500\text{--}500\text{ cm}^{-1}$ ) used in this study. This mineral can be routinely determined by FTIR techniques in the far infrared region (8). Nevertheless, the amount of material unaccounted for by the FTIR analysis is of the same order of magnitude as the concentration of pyrite determined by x-ray diffraction, strongly suggesting that by extending the spectral range of the analysis a complete determination of the major mineral components of this coal is possible. We believe the potential of this and other programs (factor analysis, etc.) for solving the problems presented by the determination of mineral matter in coal are only now being realized, but it is apparent that a good analysis of all major components can already be performed using FTIR.

#### THE QUANTITATIVE DETERMINATION OF HYDROXYL FUNCTIONAL GROUPS IN COAL

We are in the process of developing techniques to quantitatively determine functional groups present in coal. As an example we will consider the determination of -OH groups. The O-H stretching mode appears near  $3400\text{ cm}^{-1}$  in the spectra of coal. However, direct measurements of the intensity of this band cannot be used to determine such groups. A major problem is that the alkali halides used in sample preparation absorb water, which absorbs strongly in this spectral range. Some of the absorbed water appear to be in a bound state since it has been reported that heating to about  $300^\circ\text{C}$  is required for complete removal. Furthermore, coals also contain absorbed water in amounts that appear to vary according to rank and other parameters. Finally, the success of applying spectral subtraction and other procedures associated with FTIR leads us to believe that the best method for determining functional groups, particularly those containing oxygen, will prove to be a combination of chemical and FTIR procedures. For example, the infrared spectrum of a coal from Arizona is compared to the spectrum of the same sample subsequent to acetylation in Figure 4. Bands due to acetyl groups are clearly visible but it would be a difficult task to use these bands to determine the number of acetyl groups introduced and hence the number of O-H groups that have been reacted. Although suitable model compounds are available to obtain the extinction coefficients of the characteristic  $\text{C=O}$ ,  $\text{CH}_3$ , and  $\text{C-O}$  bands near  $1765$ ,  $1370$  and  $1200\text{ cm}^{-1}$  respectively, there is a major problem in measuring the intensity of these bands using traditional infrared methods because of overlap with the absorption bands of the coal. However, with FTIR we can subtract the spectrum of the unreacted material from that of the reacted to give the difference spectrum also shown in Figure 4. It can be seen that the characteristic acetyl bands are now relatively well resolved and it is a straightforward task to draw an appropriate baseline and measure peak heights or even make integrated absorption measurements. A plot of peak heights vs. concentration of coal in the KBr pellet is shown in Figure 5. The slope of these lines is equal to the extinction coefficient of the

acetyl absorption under consideration multiplied by the concentration of such groups in the coal. This latter parameter has been determined by measurements using other techniques. Consequently, this calibration allows us to use the results of this study in determining the concentration OH groups in other coals.

Acetylation usually only allows a determination of total OH content and does not allow a discrimination between phenolic and alkyl OH groups. However, using FTIR these two types of functional groups can be distinguished. Acetylation of coal OH groups leads to ester formation;



Alkyl esters normally absorb between 1720 and 1740  $\text{cm}^{-1}$ . However, when an electron withdrawing group such as an aromatic entity is attached to the single bonded oxygen this band is shifted to about 1770  $\text{cm}^{-1}$ . The strong absorption near 1765  $\text{cm}^{-1}$  in the difference spectrum shown in Figure 4 can therefore be assigned to acetyl groups that have reacted with phenolic OH, while the weaker shoulder near 1725  $\text{cm}^{-1}$  can be assigned to acetyl groups that have reacted with alkyl OH groups. We are presently investigating the use of least squares curve resolving techniques in order to obtain a measure of the relative proportions of these groups, but the potential for making such measurements is clearly outstanding.

#### VARIATIONS ON A SEAM

The variation in coal composition according to position in a seam is a problem not only in the use of this fuel in conversion processes but also in fundamental research aimed at the elucidation of structure. FTIR is particularly sensitive to small differences in materials through the use of spectral subtraction and other computer routines. We have recently examined channel samples along an exploration adit through a Canadian coking coal (14). It was determined that samples from the mouth and end of the adit showed extensive oxidation, as measured by free swelling index, while samples from near the center showed lower degrees of oxidation and still had good coking properties. The infrared spectra of several stations along the adit are shown in Figure 6. The spectra are similar and the only discernable difference involves the intensity of a shoulder near 1690  $\text{cm}^{-1}$ , which has a minimum near the center of the seam. We subtracted the spectrum of a sample from the center of the adit (70 ft) from the spectra of samples near the extremities in order to detect in more detail the chemical differences. Scale expanded difference spectra obtained by subtracting the spectrum of the 70 ft station from that of the 30 ft and 40 ft stations and the 110 ft and 125 ft stations are shown in Figure 7. These stations represent the center, mouth and end of the adit respectively. It is apparent that there are four prominent bands in the 1500 and 1800  $\text{cm}^{-1}$  region of the spectrum. Band assignments are listed in Table 3. Perhaps the most surprising is the presence of a strong band near 1585  $\text{cm}^{-1}$  characteristic of a  $\text{COO}^-$  group.

These results suggested that carbonyl and carboxyl groups were the major products of oxidation and the principal difference in these samples, according to position in the seam. This interpretation is in disagreement with other oxidation studies which have relied on chemical methods to determine groups formed upon oxidation. However, these latter studies have usually involved oxidation of a sample under laboratory conditions. There is the possibility that the  $\text{C=O}$  groups detected in this FTIR study were due to some sort of natural variability. Consequently, we applied FTIR to the characterization of coal oxidized in the laboratory. The infrared spectrum of an unoxidized coal is compared to the spectrum of the same sample oxidized for a short time at elevated temperature (about 150°C) in Figure 8. It can be seen that the major difference in the two spectra is the appearance of a shoulder near 1695  $\text{cm}^{-1}$  in the spectrum of the oxidized sample. Figure 8 also shows the difference spectrum obtained by subtracting

the spectrum of the unoxidized sample from that of the oxidized. The criteria used to determine the "correct" degree of subtraction was the elimination of the kaolinite bands at 1035 and 1010  $\text{cm}^{-1}$ , since this clay should be relatively unaffected by low-temperature oxidation. It can be seen that this subtraction results in the elimination of the aromatic C-H stretching mode near 3050  $\text{cm}^{-1}$  and the aromatic C-H out-of-plane bending mode between 700 and 900  $\text{cm}^{-1}$ . This is to be expected in that direct oxidative attack of the aromatic nuclei is unlikely under the oxidation conditions used in this study and confirms the choice of kaolinite bands as a subtraction standard.

In contrast to the aromatic C-H bands, the aliphatic C-H stretching modes near 2900  $\text{cm}^{-1}$  appear negative, or below the baseline, demonstrating a loss in  $\text{CH}_2$  groups upon oxidation. This observation is not particularly novel, as methylene groups in the benzylic position are well known to be sensitive to oxidation and are probably the initial site of oxidative attack. However, the difference spectrum reveals new detail in the 1700 to 1500  $\text{cm}^{-1}$  region of the spectrum. The 1695  $\text{cm}^{-1}$  band, which appeared as a weak shoulder in the original spectrum of the oxidized coal, is now resolved as a separate band. Furthermore, a prominent new band near 1575  $\text{cm}^{-1}$  is now revealed in the difference spectrum. This band is not detectable in the original spectrum. The 1695  $\text{cm}^{-1}$  absorption is probably due to an aryl alkyl ketone while the 1575  $\text{cm}^{-1}$  mode can be assigned to an ionized carboxyl group  $\text{COO}^-$ . Clearly, at this initial stage of the oxidation these bands represent the major products of oxidation. Weak, broad residual absorption between 1200 and 1300  $\text{cm}^{-1}$  in the difference spectrum could possibly be due to C-O bonds, as in phenols or ethers, but we would be hard pressed to identify any separately resolved bands assignable to functional groups of this type. Nevertheless, bands that can be assigned to such groups do appear at higher levels of oxidation. For example, Figure 9 compares the infrared spectrum of a coal sample, oxidized to give 6.7% oxygen uptake, to the spectrum of the unoxidized sample. The difference spectrum, obtained using the same subtraction criteria described above, is also shown in this figure. A prominent difference band can now be observed near 1200  $\text{cm}^{-1}$  bands. In addition, a weak shoulder near 1765  $\text{cm}^{-1}$  can now be resolved. This band can be assigned to an ester (see Table 3).

These spectral changes closely parallel those observed in a previous study of the variation in oxidation of coal according to position in a seam, discussed above. Consequently, the formation of carbonyl and carboxyl groups is apparently a general phenomenon during oxidation. This conclusion contradicts the results of some chemical methods of characterizing oxidation products, where no change in carboxyl or carbonyl content was detected and it was proposed that ether cross links are central to loss of swelling behavior.

## CONCLUSIONS

The results reviewed above clearly demonstrate the potential of FTIR for investigating coal structure. By applying a least squares curve fitting program and spectral subtraction methods it is possible to quantitatively determine the major mineral species present in a coal. These methods are also a sensitive probe of changes in organic structure. We have illustrated their application to the determination of hydroxyl functional groups and the formation of carbonyl and carboxyl groups during oxidation.

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TABLE 1

ANALYSIS OF MINERAL MIXTURE BY LEAST SQUARES FTIR.

<u>Mineral</u>	<u>Wt. Fraction As Prepared (%)</u>	<u>Initial Least Squares FTIR Analysis</u>	<u>Final Least Squares FTIR Analysis</u>
Kaolinite (Illinois)	50	47	46
Kaolinite (Georgia)	0	-0.3	0
Illite	0	3	0
Montmorillonite	25	31	24
Mica/Montmorillonite	25	29	30
Quartz	0	-9	0
Calcite	0	-0.2	0

TABLE 2

ANALYSIS OF LOW TEMPERATURE ASH  
(ILLINOIS #6 COAL, 'ROUND ROBIN' SAMPLE)

Mineral	Wt. Fraction By FTIR Least Squares Analysis 1	Wt. Fraction By FTIR Least Squares Analysis 2	Wt. Fraction By X-ray And Conventional IR Methods %
Kaolinite (Illinois)	-12	0	13.5
Kaolinite (Georgia)	20	13	
Quartz	24	25	20
Calcite	6	7	6
Pyrite	N/D	N/D	20
Montmorillonite	21	18	N/D
Mica/Montmorillonite	16	9	
Illite	-6	0	
TOTAL	69%	72%	59.5%
UNACCOUNTED FOR	31%	28%	40.5%

N/D - not determined.

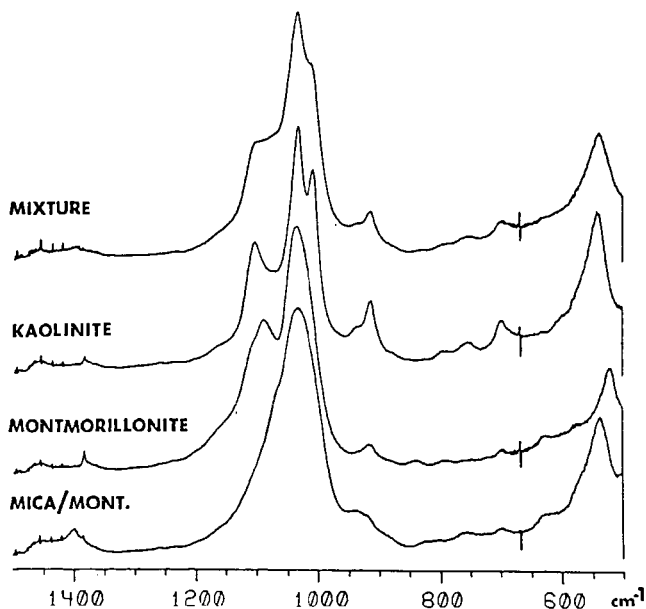


Figure 1: Scale expanded FTIR spectra in the range 500-1500  $\text{cm}^{-1}$  of three clays, mica-montmorillonite, montmorillonite and kaolinite. The spectrum shown at the top is that of 1:1:2 mixture by weight of the three clays respectively.

TABLE 3

## BAND ASSIGNMENTS FOR THE INFRARED SPECTRA OF COALS

ALIPHATIC AND AROMATIC GROUPS		OXYGEN CONTAINING FUNCTIONAL GROUPS	
Wave Number cm <sup>-1</sup>	ASSIGNMENT	Wave Number cm <sup>-1</sup>	Assignment
		3300	Hydrogen Bonded
3030	Aromatic C-H		
2950 sh	CH <sub>3</sub>		
2920 } 2850 }	{ Aliphatic -CH CH <sub>2</sub> and CH <sub>3</sub>		
		1835	C = O, Anhydride
		1775-1765	C = O, Ester with Electron withdrawing group attached to single bonded oxygen $\text{Ar} - \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{R}$
		1735	C = O, Ester
		1690-1720	C = O, Ketone, Aldehyde and, -COOH
		1650-1630	C = O Highly Conjugated $\text{eg Ar} - \overset{\text{O}}{\parallel} \text{C} - \text{Ar}$
1600	Aromatic Ring Stretch	Approx. 1600	Highly Conjugated Hydrogen Bonded C = O
		1560-1590	Carboxyl Group in Salt Form -COO <sup>-</sup>
1490 sh	Aromatic Ring Stretch		
1450	CH <sub>2</sub> and CH <sub>3</sub> Bend Possibility of Some Aromatic Ring Modes		
1375	CH <sub>3</sub> Groups		
		1330 to 1110	C-O Stretch and O-H Bend in Phenoxy Structures, Ethers.
		1100-1000	Aliphatic Ethers, Alcohols.
900-700	Aromatic C-H out-of-plane bending modes		
860	Isolated Aromatic H		
833 (Weak)	1,4 Substituted Aromatic Groups		
815	Isolated H and/or 2 Neighboring H		
750	1,2 Substituted ie 4 Neighboring H		



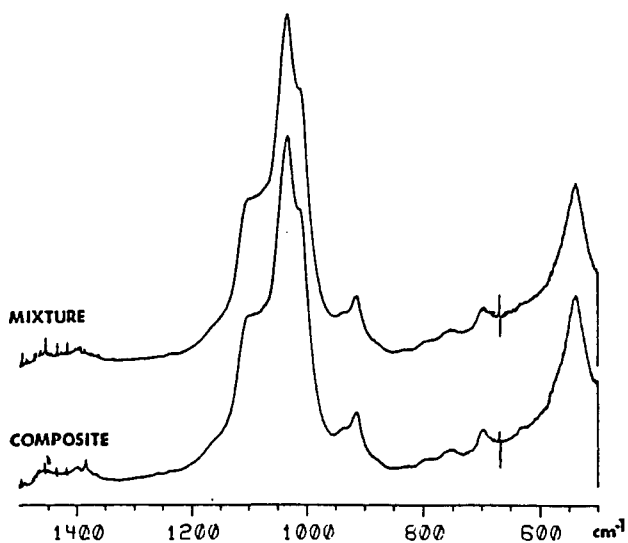


Figure 2: Scale expanded FTIR spectra in the range 500-1500  $\text{cm}^{-1}$ .

Top: Mineral mixture of mica/montmorillonite, montmorillonite and kaolinite (1:1:2 by weight).  
 Bottom: Composite spectrum synthesized from the least squares fitting program.

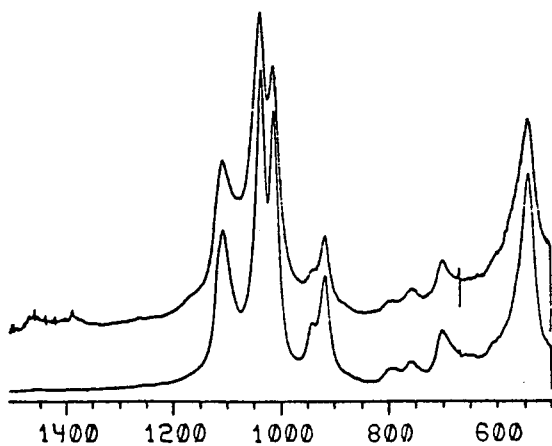


Figure 3: FTIR spectra in the range 500-1500  $\text{cm}^{-1}$  of kaolinite standards

Top: Illinois.  
 Bottom: Georgia.

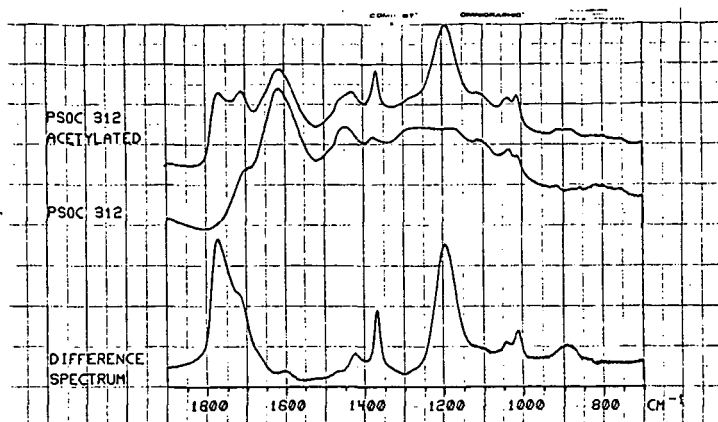


Figure 4: Top: FTIR Spectrum of acetylated coal  
 Middle: FTIR spectrum of original coal (PSOC 312)  
 Bottom: Difference spectrum

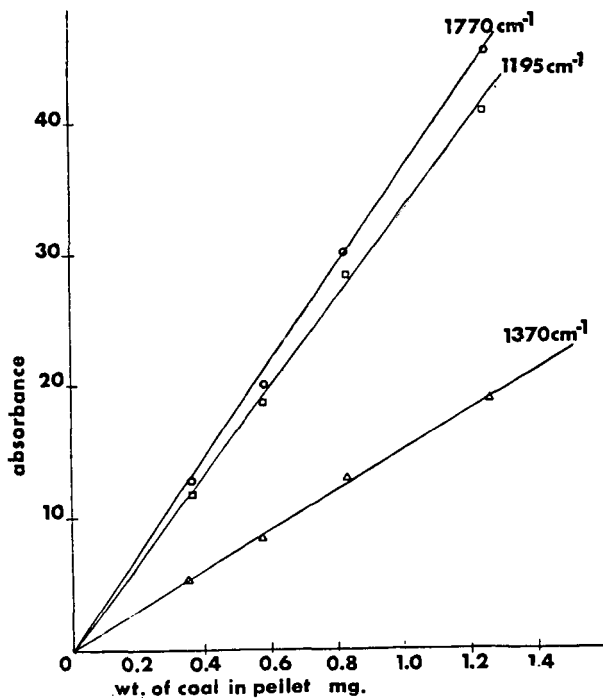


Figure 5: Plot of peak height of 1765; 1370 or 1195 cm⁻¹ bands vs. concentration of coal in KBr pellet. (Measurements made on difference spectra)

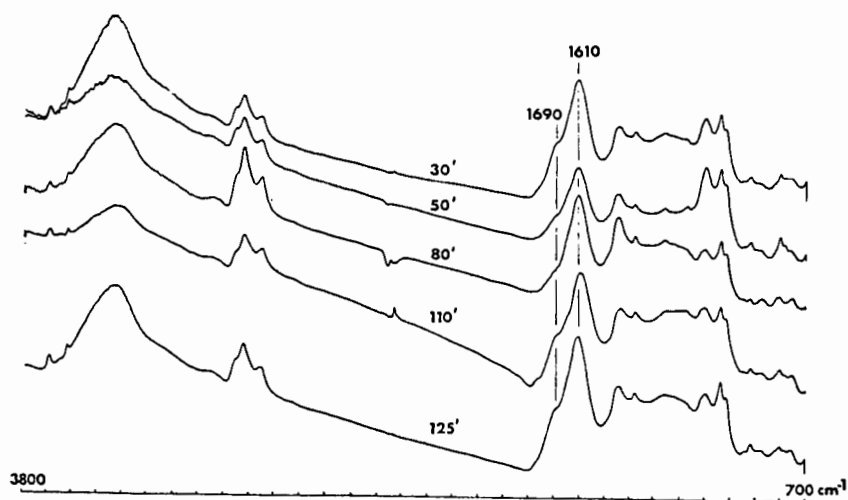


Figure 6: Infrared spectra of selected coal samples from stations along the seam.

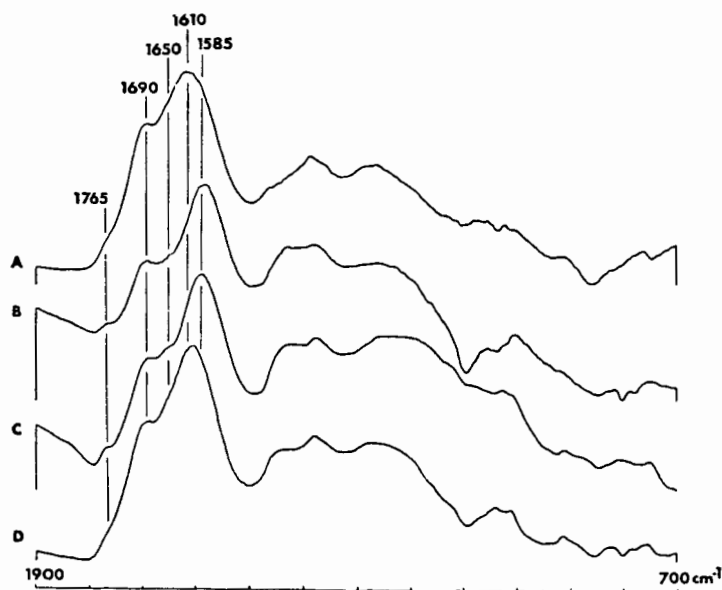


Figure 7: Difference spectra obtained by subtracting spectrum of coal from 70 ft. station from spectra of coals from A. 30 ft., B. 40 ft., C. 110 ft., and D. 125 ft.

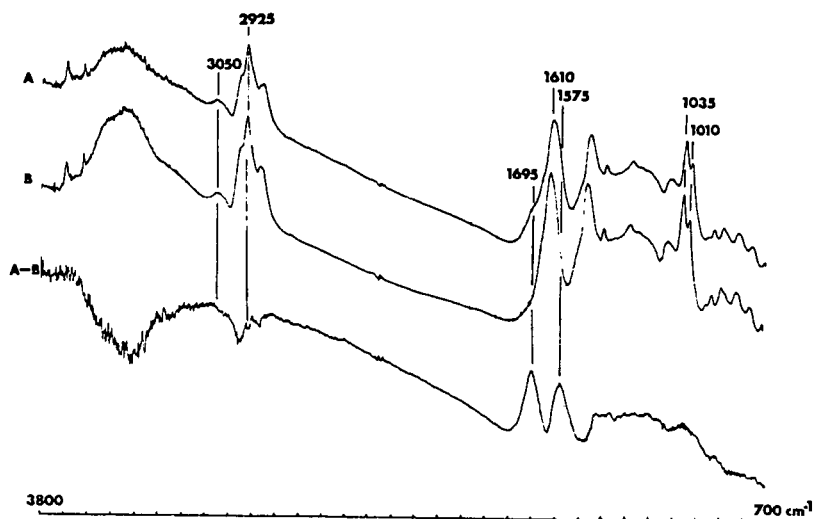


Figure 8: FTIR spectra in the range 700-3800  $\text{cm}^{-1}$ .  
 A. Coal sample slightly oxidized at 150°C.  
 B. Unoxidized coal.  
 A-B. Difference spectrum.

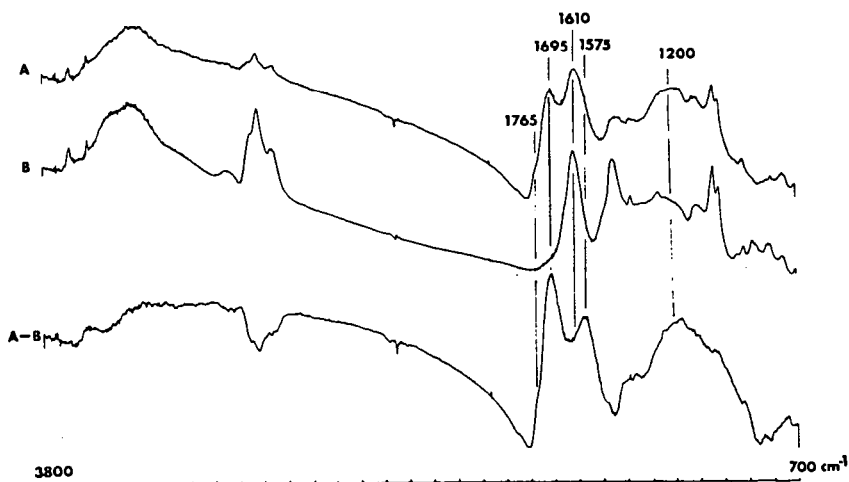


Figure 9: FTIR spectra in the range 700-3800  $\text{cm}^{-1}$ .  
 A. Oxidized coal (6.7%  $\text{O}_2$  uptake).  
 B. Unoxidized coal.  
 A-B. Difference spectrum.